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On shape variation of confined triatomics of XY_2-type

U. Müller-Herold[a]

ETH Zurich, P.O. Box CAB 24, CH-8092 Zurich, Switzerland

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Abstract. Harmonic confinement of initially isolated symmetric triatomic molecules can induce a transition from a bent, directed bond-type structure to helium-like angular correlation of the two equal particles. In an exactly solvable modification of the Hooke-Calogero model it is demonstrated that there is a well-defined transition between the two cases if the confinement strength is increased. Furthermore confinement is shown to reduce the system's effective diameter, which at the transition point has shrunk by 26% in comparison to the isolated system.

PACS. 31.70.Dk Environmental and solvent effects – 33.15.Dj Interatomic distances and angles – 03.65.Ge Solutions of wave equations: bound states – 68.65.Hb Quantum dots (patterned in quantum wells)

1 Introduction

Historically, most work in quantum chemistry deals with single molecules in empty Euclidean space. If, in addition, interactions with the environment are considered on a fundamental level, the quantized electromagnetic field is the universal background structure to be taken into account. On a more phenomenological level, various kinds of model interactions have been used for the treatment of solvent effects, for the interaction with external classical electromagnetic fields as in spectroscopy and for many others.

A related concept is the confinement of electrons in so-called quantum dots in semiconductor physics. The observed properties of these confined electrons are similar to those of electrons in atoms. Most work on quantum dots is based on a model in which the effective electron motion is two-dimensional and the space occupied by the electrons in these two dimensions is restricted by a confining potential [1,2]. Additionally, there is some work that includes three-dimensional electron motion [3]. Usually, the confining potential is parabolic and the electrons interact via Coulomb repulsion. Frequently, the physics of the system under observation is well reproduced by the two-dimensional parabolic model [4]. This makes exploring the effects of confining parabolic potentials in the molecular domain promising.

Here in particular we report on the influence of confinement on molecular shape. In a previous paper [5] it was shown how nuclear masses can influence the shape of triatomic molecules. More precisely, it was demonstrated in the Hooke-Calogero model of a triatomic of XY_2-type that variation of the masses can induce transitions from a bent "molecular geometry" to more diffuse "helium-like" states. The present contribution's objective is to show that for given nuclear masses and interparticle potentials external confinement can generate similar changes.

The Hooke-Calogero Hamiltonian for triatomic molecules belongs to a class of three-particle Hamiltonians where attracting forces are harmonic. Sometimes these models are solvable for all values of the model parameters. In other cases they can be quasi-solvable in the sense that there exists a discrete set of numerical values of the model parameters for which analytical solutions can be found. If all interactions are given by harmonic potentials one has what is called the Moshinsky model [6]. By contrast, harmonic attraction in combination with Coulombic repulsion is characteristic for the harmonium model (or Hooke's law atom or simply hookium) [7]. The harmonium model is quasi-solvable [8] and its main application is the testing of density functionals. If furthermore Coulombic repulsion in harmonium is replaced with an inverse square potential (well-known from centrifugal distortion) one arrives at the solvable Hooke-Calogero model [9,10]. Recently this model was extended to four particles in order to obtain an analytical non-Born-Oppenheimer wave function for the H_2 molecule [11].

The nuclear Hamiltonian of the isolated Hooke-Calogero triatomic is defined as

$$\hat{H}_{mol} = -\frac{1}{2m_e}\Delta_{\vec{Q}_1} - \frac{1}{2m_e}\Delta_{\vec{Q}_2} - \frac{1}{2m_u}\Delta_{\vec{Q}_3} + V \quad (1)$$

$$V = \frac{1}{2}\left(\vec{Q}_3 - \vec{Q}_1\right)^2 + \frac{1}{2}\left(\vec{Q}_3 - \vec{Q}_2\right)^2 + \frac{1}{(\vec{Q}_2 - \vec{Q}_1)^2} + \frac{g}{4}\left(\vec{Q}_2 - \vec{Q}_1\right)^2 \quad (2)$$

[a] e-mail: mueller-herold@env.ethz.ch

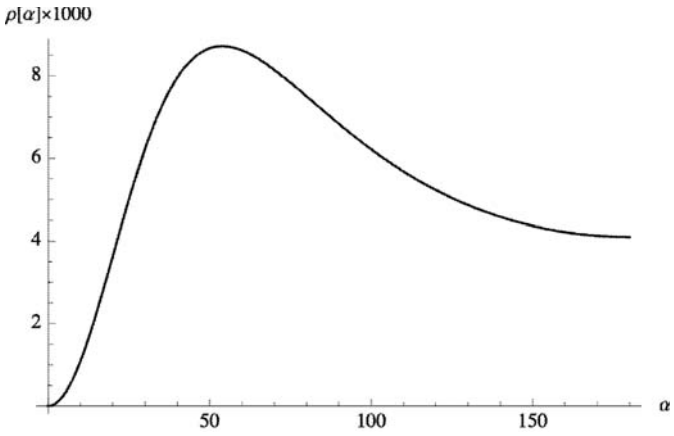

Fig. 1. Probability distribution for the Y-X-Y angle α (degrees) in the ground state of an isolated XY_2 triatomic in the Hooke-Calogero model. The maximum at $\alpha = 53.9°$ is identified with the bond angle. (The numerical values of the model parameters are the ones fixed in Sect. 1.)

where $\vec{Q}_1$, $\vec{Q}_2$ and m_e are the coordinates and the mass of the two equal Y nuclei, whereas $\vec{Q}_3$ and m_u are the coordinates and the mass of the third "unequal" X nucleus. As in atomic units Planck's constant is unity. The Y mass is set to $m_e = 2$ and the X mass is assumed to be $m_u = 32$. The parameter g – tuning the Y-X-Y angle – is set to 15. In Jacobi coordinates

$$\begin{pmatrix} \vec{r}_1 \\ \vec{r}_2 \\ \vec{r}_3 \end{pmatrix} = \begin{pmatrix} -1 & 1 & 0 \\ -1/2 & -1/2 & 1 \\ m_e/M & m_e/M & m_u/M \end{pmatrix} \begin{pmatrix} \vec{Q}_1 \\ \vec{Q}_2 \\ \vec{Q}_3 \end{pmatrix} \quad (3)$$

the Hamiltonian reads

$$\hat{H}_{mol} = -\frac{1}{m_e}\Delta_{\vec{r}_1} - \frac{1}{2\mu}\Delta_{\vec{r}_2} - \frac{1}{2M}\Delta_{\vec{r}_3} + \frac{1+g}{4}\vec{r}_1{}^2 + \frac{1}{\vec{r}_1{}^2} + \vec{r}_2{}^2 \quad (4)$$

where $M = 2m_e + m_u = 36$ denotes the total mass and $\mu = 2m_e m_u/(2m_e + m_u) = 32/9$ is the reduced mass of the three-body system. With these parameter values the Hooke-Calogero triatomic has a V-shaped ground state with a Y-X-Y angle of 53.9° (Fig. 1).

2 Confinement

In contrast to solids, confinement in liquids does not localize the object under consideration in a fixed spatial domain but in a "cage" moving together with the confined object. Accordingly, confining potentials in liquids should not act on the object's center-of-mass coordinate, but only on the relative coordinates in the center-of-mass system. For the Hooke-Calogero Hamiltonian (Eqs. (1) and (2)) and parabolic confinement the potential is chosen as

$$\begin{aligned} V_{conf} &= \frac{f'}{2}\left\{ m_e^2\left(\vec{Q}_1 - \vec{r}_3\right)^2 + m_e^2\left(\vec{Q}_2 - \vec{r}_3\right)^2 \right. \\ &\quad \left. + m_u^2\left(\vec{Q}_3 - \vec{r}_3\right)^2 \right\} \\ &= \frac{f}{2}\left\{ \frac{\vec{r}_1^{\,2}}{2} + \frac{6m_u^2}{M^2}\vec{r}_2^{\,2} \right\} \end{aligned} \quad (5)$$

where $f := f' m_e^2$ denotes the confinement strength and

$$\begin{pmatrix} \vec{Q}_1 \\ \vec{Q}_2 \\ \vec{Q}_3 \end{pmatrix} = \begin{pmatrix} -1/2 & -m_u/M & 1 \\ 1/2 & -m_u/M & 1 \\ 0 & 2\,m_e/M & 1 \end{pmatrix} \begin{pmatrix} \vec{r}_1 \\ \vec{r}_2 \\ \vec{r}_3 \end{pmatrix}. \quad (6)$$

The confined molecule's total Hamiltonian $\hat{H} = \hat{H}_{mol} + \hat{V}_{conf}$,

$$\hat{H} = -\frac{1}{m_e}\Delta_{\vec{r}_1} - \frac{1}{2\mu}\Delta_{\vec{r}_2} - \frac{1}{2M}\Delta_{\vec{r}_3} + \frac{1+g}{4}\vec{r}_1^{\,2} + \frac{1}{\vec{r}_1^{\,2}} + \vec{r}_2^{\,2} + \frac{f}{2}\left\{ \frac{\vec{r}_1^{\,2}}{2} + \frac{6m_u^2}{M^2}\vec{r}_2^{\,2} \right\} \quad (7)$$

is the sum of three commuting parts which after subtraction of the center-of-mass term give the internal Hamiltonian $\hat{H}_{int} =: \hat{H} + \Delta_{\vec{r}_3}/2M = \hat{H}_1 + \hat{H}_2$ with

$$\begin{aligned} \hat{H}_1 &=: -\frac{1}{m_e}\Delta_{\vec{r}_1} + \frac{1+g+f}{4}\vec{r}_1^{\,2} + \frac{1}{\vec{r}_1^{\,2}} \\ &= -\frac{1}{2}\Delta_{\vec{r}_1} + 4\,\vec{r}_1^{\,2} + \frac{f}{4}\vec{r}_1^{\,2} + \frac{1}{\vec{r}_1^{\,2}} \end{aligned} \quad (8)$$

$$\begin{aligned} \hat{H}_2 &=: -\frac{1}{2\mu}\Delta_{\vec{r}_2} + \vec{r}_2^{\,2} + \frac{f}{2}\frac{6m_u^2}{M^2}\vec{r}_2^{\,2} \\ &= -\frac{9}{64}\Delta_{\vec{r}_2} + \vec{r}_2^{\,2} + \frac{f}{2}\frac{128}{27}\vec{r}_2^{\,2} \end{aligned} \quad (9)$$

and corresponding non-normalized ground-state wave functions

$$\Psi_{1,0}(r_1) = r_1\, e^{-a r_1^2/4} \quad (10)$$

$$\Psi_{2,0}(r_2) = e^{-b\, r_2^2} \quad (11)$$

where

$$a =: 2\sqrt{8 + f/2} \quad \text{and} \quad b =: \sqrt{(8/9)(2 + 128f/27)}. \quad (12)$$

In order to extract molecular shape from the wave function we proceed along the lines of reference [5]: from the ground-state density

$$\left(\Psi_{1,0}\Psi_{1,0}^*\right)(\vec{r}_1)\left(\Psi_{2,0}\Psi_{2,0}^*\right)(\vec{r}_2) := |r_1|^2 e^{-a\, r_1^2/2}\, e^{-2\, b\, r_2^2} \quad (13)$$

we calculate the expectation value of the two-density operator

$$\begin{aligned} \hat{\rho}'(\vec{q}_1, \vec{q}_2) &= \delta(\vec{Q}_3 - \vec{Q}_1 - \vec{q}_1)\,\delta(\vec{Q}_3 - \vec{Q}_2 - \vec{q}_2) \\ &= \delta(\vec{r}_2 - \vec{r}_1/2 - \vec{q}_1)\,\delta(\vec{r}_2 + \vec{r}_1/2 - \vec{q}_2) \end{aligned} \quad (14)$$

which gives

$$\rho'(\vec{q}_1,\vec{q}_2) \propto |\vec{q}_1-\vec{q}_2|^2\, e^{-a(\vec{q}_1-\vec{q}_2)^2/2}\, e^{-b(\vec{q}_1+\vec{q}_2)^2/2} \quad (15)$$

where the proportional sign ($\propto$) is used to omit unnecessary factors. The probability of finding the two Y nuclei at a distance q from the X nucleus in a shell of thickness dq is proportional to

$$dqq^2\rho'(\vec{q_1},\vec{q_2})_{q_1=q_2=q} = dqq^4(2-2\cos\alpha)e^{-aq^2(1-\cos\alpha)}e^{-bq^2(1+\cos\alpha)} \quad (16)$$

where α is the Y-X-Y angle. Integration over q now leads to the distribution

$$\rho(\alpha) \propto \int_0^\infty dq\, q^2\rho'(\vec{q}_1,\vec{q}_2)_{q_1=q_2=q} = \frac{(1-\cos\alpha)}{(a(1-\cos\alpha)+b(1+\cos\alpha))^{5/2}} \quad (17)$$

which for the isolated molecule (i.e. for $f = 0$) is shown in Figure 1. It shows two minima at $\alpha = 0°$ and $\alpha = 180°$ resp. and an intermediate maximum at $\alpha = 53.9°$ corresponding to the bond angle of a V-shaped triatomic such as H_2O, NO_2 or SO_2.

3 Shape variation under changing confinement strength

The maximum of the angular distribution equation (17) corresponding to the Y-X-Y angle is given by

$$\cos\alpha = 1 - \frac{4}{3}\frac{1}{a(f)/b(f)-1}. \quad (18)$$

With increasing confinement strength f the maximum shifts towards higher values of α and becomes flatter. At $f = 2.79$ it merges with the former minimum at $\alpha = 180$ (Fig. 1) and for $f \geq 2.79$ the angular distribution function takes a helium-like form: a minimum at $\alpha = 0$ (corresponding to the Coulomb hole) and a monotonic increase leading to a flat diffuse maximum at $\alpha = 180$ (Fig. 2).

The main difference with respect to Coulombic helium is the absolute value at the minimum at $\alpha = 0$: in the Hooke-Calogero model $\rho(0)$ is exactly zero, whereas for helium the Coulomb hole is less deep: $\rho(0) > 0$ (Fig. 3).

Confinement compresses the system. This can be seen from the expected value E_Y of the Y density in center-of-mass coordinates

$$E_Y = \frac{2(3a+2b'')\sqrt{2/\pi}}{3\sqrt{a\,b''}\sqrt{(2a+b'')}} \quad (19)$$

where $b'' = 2\,b\,M^2/m_u^2 = 2\sqrt{(8/9)(2+128f/27)}\,(81/64)$ (see Appendix, Eq. (A.6)). E_Y is the effective radius of the system. For increasing confinement strength f the effective radius monotonically decreases from 0.75 at $f = 0$. At the transition point from a bent to a helium-like structure, i.e. at $f = 2.79$, the effective radius has shrunk to 0.56 (Fig. 4).

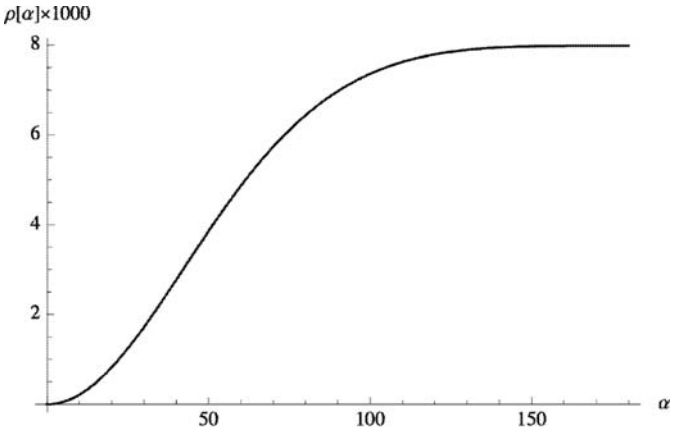

Fig. 2. The probability distribution of the Y-X-Y angle α (degrees) in the ground state of a confined XY_2 triatomic in the Hooke-Calogero model at confinement strength $f = 2.79$ shows a helium-type angular correlation.

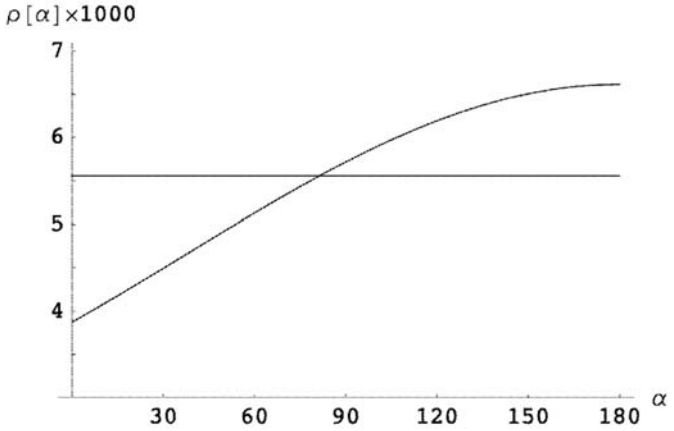

Fig. 3. Angular correlation of Coulombic helium as calculated from the nearly exact Hylleras wave function of the electronic ground state. The straight horizontal line at 5.56 represents the $(1s)^2$ situation of Hartree-Fock-type uncorrelated wave functions (from Ref. [5]).

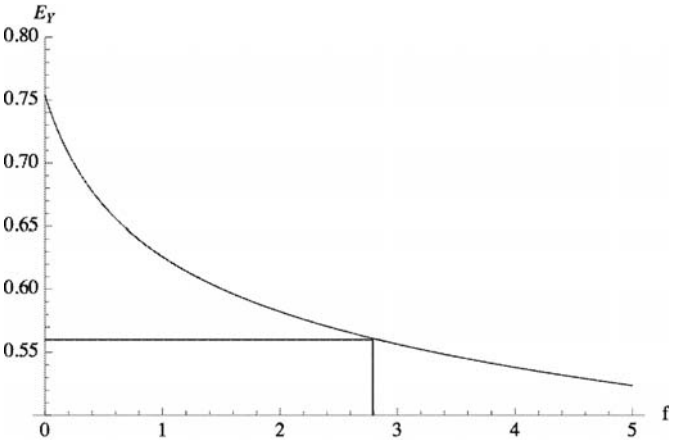

Fig. 4. Shrinking of the effective radius E_Y with increasing confinement strength f. At $f = 2.79$, where the transition to helium-like angular correlation occurs, the system has lost 26% of its original diameter.

4 Concluding remarks

The Hooke-Calogero model demonstrates that in special cases molecular objects can change their shape under confinement. However, the model is restricted to "harmonic" attraction between the unequal particles and one may ask what this implies for "real" Coulombic systems. A first hint can be found in the detailed comparison of Coulombic helium and its Hookean counterpart due to O'Neil and Gill. They found that although Hookean and Coulombic helium are quantitatively different – hookium being a more diffuse species, and the overlap of the two ground-state wave functions being ~ 0.6 – meaningful qualitative comparisons can be made between the two [12]. That hookium is more diffuse than Coulombic helium intuitively derives from characteristic differences between Coulomb and oscillator forces: the former are strong at short distances and weak at longer distances whereas the latter behave conversely. Accordingly, the asymptotic decay of particle densities in Coulombic systems is slow (exponential [13]) while it is fast (Gaussian) in the Hookean case. For short distances, however, harmonic attraction is comparatively weak. This leads to the overall picture that hookium is locally more diffuse but asymptotically more contracted than its Coulombic counterparts. Since these considerations equally apply to inverse square potentials, the qualitative similarities and dissimilarities between Coulombic and Hookean three-particle systems are expected to be likewise valid for the Calogero variant.

A further question concerns the theoretical status of helium-like angular correlation. In principle, electronic angular correlation as depicted in Figure 3 seems to coincide with proton angular correlation in large amplitude bending modes of linear triatomics such as BeH_2. At first sight, from a purely mathematical point of view, there seems to be no difference between the two. From a physical perspective, on the other hand, large amplitude bending occurs in highly excited vibrational states, whereas in Coulombic helium or in the Hooke-Calogero triatomic it occurs in the ground state. According to this there should be no confusion in practice. In a broader theoretical setting, however, it is tempting to reverse the question: is there really a fundamental difference between electronic angular correlation in the ground state of helium and protonic angular correlation in higher excited vibrational states of linear first row hydrides such as BeH_2? In other words: do there exist helium-like excited proton states in first row dihydrides? This presents an intricate problem since the Born-Oppenheimer approximation for protons is no longer reliable in these cases (which can be seen from the Renner-Teller effect in some of these molecules [14,15]).

Definite answers for Coulombic systems will probably only be obtained if electrons and Y particles such as the protons in the first row dihydrides are treated on the same computational footing; i.e. without clamping the Y particles at some stage when dealing with the electrons. Molecular structure calculations without clamping the nuclei are a formidable task, far from any kind of ready-to-use procedure (for a review cf. the extended overviews by Cafiero et al. [16] and Sutcliffe and Woolley [17]). The water molecule, for example, is a quantum mechanical thirteen-particle problem which is beyond the scope of genuine non-BO-methods such as the stochastic variational method by Varga and Suzuki [18] that has never been applied to systems with more than 6 particles. Moreover, since the effect sought-after is a subtle one, one needs exact or nearly exact solutions which excludes bold approximations.

Appendix: Y density

For the calculation of molecular size we start with the calculation of the Y density in center-of-mass coordinates. In the ground state (Eqs. (10)–(12)) the expectation value of the corresponding one-density operator

$$\begin{aligned}\hat{\rho}(\vec{q}) &=: \delta(\vec{Q}_1 - \vec{r}_3 - \vec{q}) + \delta(\vec{Q}_2 - \vec{r}_3 - \vec{q}) \\ &= \delta(\vec{r}_1/2 + \vec{r}_2 m_u/M + \vec{q}) + \delta(\vec{r}_1/2 - \vec{r}_2 m_u/M - \vec{q})\end{aligned} \tag{A.1}$$

is given by

$$\rho(\vec{q}) \propto \int_{\mathbb{R}^3} d^3r_1 \int_{\mathbb{R}^3} d^3r_2 \hat{\rho}(\vec{q}) |r_1|^2 e^{-a\, r_1^2/2}\, e^{-2b\, r_2^2}, \tag{A.2}$$

with

$$\begin{aligned}\int_{\mathbb{R}^3} d^3r_2 (\delta(\vec{r}_1/2 + \vec{r}_2 m_u/M + \vec{q}) + \delta(\vec{r}_1/2 - \vec{r}_2 m_u/M - \vec{q})) \\ e^{-2b\, r_2^2} = e^{-b''(r_1^2/4 + \hat{q}^2)} \cosh(b'' \vec{r}_1 \vec{q})\end{aligned} \tag{A.3}$$

and $b'' =: 2bM^2/m_u^2 = 2\, b(81/64)$ it follows

$$\rho(\vec{q}) \propto \int_{\mathbb{R}^3} d^3r_1 |r_1|^2 e^{-a\, r_1^2/2} e^{-b''(r_1^2/4 + \hat{q}^2)} \cosh(b'' r_1 q\, \cos[\beta]) \tag{A.4}$$

where $\cos[\beta] = \vec{r}_1 \vec{q}/r_1 q = \cos\, \vartheta_1 \cos\vartheta + \sin\vartheta_1\, \sin\vartheta \cos(\varphi_1 - \varphi)$ is the angle between $\vec{r}_1 = (r_1, \vartheta_1, \varphi_1)$ and $\vec{q} = (q, \vartheta, \varphi)$. Due to the spherical symmetry it suffices to calculate the q-dependence of ρ in one direction. The most convenient choice is $\sin\vartheta = 0$ which gives

$$\begin{aligned}\rho(q) &\propto \int_0^\infty d^3r_1 |r_1|^4 e^{-a\, r_1^2/2} e^{-b''\,(r_1^2/4 + q^2)} \\ &\quad \times \int_0^\pi \sin\vartheta_1 d\vartheta_1 \cosh(b'' r_1 q\, \cos\vartheta_1) \\ &\propto \frac{e^{-b'' q^2}}{b'' q} \int_0^\infty d^3r_1 |r_1|^3 e^{-\frac{1}{4}(2a + b'') r_1^2} \sinh(b'' r_1 q\, \cos\vartheta_1) \\ &\propto \frac{4\sqrt{\pi}(6a + b''(3 + 2b'' q^2))}{(2a + b'')^{7/2}} \exp\left\{-\frac{2a\, b'' q^2}{2a + b''}\right\}.\end{aligned} \tag{A.5}$$

After normalization of the density distribution equation (A.5) the expectation value of the Y density reads

$$E_Y := \int_0^\infty dq\, \rho(q)\, q^2 q = \frac{2(3a+2b'')\sqrt{2/\pi}}{3\sqrt{a\,b''}\sqrt{(2a+b'')}}. \qquad \text{(A.6)}$$

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